RECOVERY and PURIFICATION of NICKEL SALTS and CHROMIC ACID using the RECOFLO SYSTEM

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1. Introduction

In a plating shop there are opportunities to recycle chemicals without sacrificing product quality. In fact, a well designed system can actually help a plater maintain cleaner, more productive solutions.

Since 1975, several systems using the patented Recoflo® ion exchange process have been successfully operated to reclaim and purify plating chemicals. This paper will discuss two specific applications of the Recoflo® process, recovery of nickel salts and chromic acid.

2. Nickel salt recovery

Nickel plating tanks are followed by several counterflowing rinse tanks to prevent contamination of subsequent chrome plating solutions. Plated parts typically carry out 0.1 L/m^2 of plating solution into the rinses. In many plants this dragout solution ends up as a hazardous waste sludge that must be transported and disposed in a secure landfill.

In addition to the loss of material, the costs of removing the nickel from the rinse water can be substantial:

i) nickel is a toxic heavy metal, requiring chemical treatment and precipitation,
ii) sludge produced is considered to be hazardous and must be stored in a secure landfill,
iii) labor is required for treatment and disposal,
iv) there is a long term liability associated with the disposal of hazardous wastes.

These economic and legal considerations, coupled with a desire to be environmentally responsible, lead many platers to recover and recycle nickel salts from rinsing wastes.

2.1 Production considerations

Key objectives for most platers include the need to get production out on time, to meet or exceed customer expectations and to keep production costs within budget. The purpose of a recycling strategy is to reduce production costs. Recycling chemicals can, however, lead to troubles with the plating solutions if care is not taken with the design and operation of the system. A number of factors must be considered.

i) ***Purity*** - Contaminants that have accumulated in the rinse tanks should be removed before the nickel solution is recycled to the plating bath. If not, these recycled contaminants would buildup in the bath and cause an adverse effect on the plating quality and bath life.

ii) ***Brighteners -*** Brighteners are usually sodium-salts of organic compounds and they are consumed / degraded in the plating process or lost to dragout. Dragout actually provides an important outlet for degraded brighteners and sodium. While recycling brighteners might appear to be beneficial, four problems can be encountered:

- degraded brighteners are recovered, increasing the load on carbon filters,
- some decanting of the tank may be required to control sodium levels,
- brightener control is difficult when a portion of the brightener package is recycled,
- salts recycled to the semi-bright tanks cannot contain brighteners.

iii) ***Composition*** - The recovered solution should be sufficiently concentrated so that the volume can be returned to the plating tank without the need for additional evaporation equipment. A nickel concentration of 30-40 g/L is usually sufficient. As the nickel exists as both a chloride and sulfate salt in the plating tank, it is preferable to recover it in this mixed form.

iv) ***pH*** - The pH of the recycled nickel solution should be in the correct range to facilitate direct return to the plating bath. Adjustment enters unwanted chemicals to the bath.

v) ***Concentration*** - In duplex nickel plating systems, it is common for plated parts to move from the semi-bright tank to the bright tank without an intermediate rinsing step. As the nickel salt contents of the two tanks are similar, the dragout from the semi-bright tank replenishes the salt content in the bright tank. Nickel salts recovered from the rinses after the bright tank must be recycled to the semi-bright tank.

When nickel plating consists of a bright tank only, the salt content of the tank will gradually decline due to dragout. This fact, combined with the evaporative losses from the tank, makes it possible to recycle most or all of the recovered nickel salts.

Care must be taken, however, as anodes typically operate at higher current efficiencies than cathodes. This means that, if all the dragout is recycled, the salt level in the tank can gradually increase. This can be controlled with the use of specially designed, insoluble anodes.

2.2 Nickel recovery alternatives

There are a number of separation processes which have been used to recover nickel salts.

i) ***Evaporation*** - Simple humidification-type evaporators can be attached to the plating tank, or self-sufficient steam-fired units can be used to concentrate the nickel rinse water. Evaporation can usually recover over 90% of the dragout, provided there are enough rinse tanks to ensure good cleaning of the parts before chrome plating. Evaporators are simple to operate, can be very inexpensive to purchase, and can provide a very concentrated (>40 g/L) product. The main drawback to evaporation is that all dissolved materials (including degraded brighteners, sodium and tap-water contaminants) are recovered, making recycle difficult.

ii) ***Reverse osmosis*** - Rinse water is pressurized against a semi-permeable membrane that rejects almost all dissolved materials, including organic brighteners. These units can treat larger volumes, making rinsing much easier, while recovering >95% of the nickel salts. While often more expensive than some evaporators, reverse osmosis (RO) units can produce a fairly concentrated 10-20 g/L product. The main weakness with RO is membrane life, inability to reduce nickel to low ppm levels in the reject, and sodium / brightener recovery in the product.

iii) ***Electrodialysis*** - Rinse water is pumped through a stack of ion-selective membranes that allow nickel, sodium and other cations to pass through when an electrical current is applied. Nickel passes into an acid solution, which must be neutralized to the proper pH for reuse. Over 99% of the nickel can be recovered and treating relatively large volumes is possible. Membrane life and serviceability can be a concern with electrodialysis systems.

iv) ***Ion exchange*** - Ion exchange uses a column of chemically active resin beads that exchange hydrogen for nickel. Acid regeneration of the resin yields a relatively concentrated nickel salt solution, with >97% of the nickel from the rinse water. Ion exchange can economically treat large volumes of rinse water and remove nickel to very low part-per-million (ppm) levels. The excess acid in the recovered nickel salts must be neutralized to the proper pH for reuse. Also, the acidic, nickel-free rinse water must be neutralized prior to discharge.

v) ***Electrowinning*** - In addition to the above, electrowinning has been used to a limited degree. A modified plating process is used to reduce nickel levels in the rinse water. There are a number of problems with this method, including:

- inability to plate out nickel to ppm levels,
- difficulty in harvesting and reusing nickel metal,
- recovery of brightener compounds in metal,
- complex equipment design.

Table 1 summarizes the capabilities of these processes.

2.3 The advanced Recoflo® System for nickel recovery

Originally commercialized in 1970, patented Recoflo ion exchange technology has been used for a wide variety of chemical recovery applications. Recoflo is characterized by its use of:

i) fine mesh resin,
ii) fully-packed resin columns,
iii) counter-current regeneration,
iv) short resin columns.

The Recoflo System is a pre-assembled, skid mounted device that is fully tested, prior to shipment. The resin columns are mounted on an epoxy coated steel frame with process valves, internal piping and a control panel.

When designed for nickel recovery, the Recoflo method immediately offers a significant improvement in nickel removal efficiency and product concentration (up to 40 g/L as nickel). More importantly, the Recoflo System offers a number of other important features. Specifically, the System is designed to:

i) reject organic brighteners.....it has been approved by OEM parts suppliers for duplex nickel,
ii) reject sodium.....gradual accumulation in the plating tank does not occur,
iii) regenerate with sulfuric and hydrochloric acid.....recovered salts match the tank chemistry,
iv) remove and reuse excess acid from the recovered salt.....recycling does not upset bath pH,

v) incorporate specially designed, insoluble anodes.....nickel plating balances anode dissolution, ensuring that all recovered salts can be reused.

The S.T.E.P. (Simultaneous Thickness and Electrochemical Potential) test, developed by Enthone-EMI, is a widely accepted quality assurance rating for duplex nickel coatings in the automotive industry. Automotive OEMs are mandated to have S.T.E.P. readings of 100 mV or greater on their final plated product.

S.T.E.P. test results were collected on a duplex nickel plating tank from a long time user (16 years) of a Recoflo System. As can be seen from the data in Figure 1, the S.T.E.P. results clearly indicate that recycling nickel salts recovered from the Recoflo System had no adverse effects on the quality of the plated parts.

By ensuring that all the salts recovered can be safely and fully recycled, the Recoflo System for nickel recovery can reduce related operating costs by over 90% and recover over 99% of the nickel. See Table 2.

Danaher Inc., located in the United States, has been the primary supplier of brand name hand tools for Sears & Roebuck since 1938. Danaher has eight plating tanks with approximately 53,000 liters of semi-bright and bright plating solution. In mid-1996, Danaher Tool Group became concerned about the nickel waste emanating from in its North Carolina Operation. Without any metal reclaiming system in use, nickel drag-out from Danaher's plating tanks averaged 55.5 kg per day. Not only was this waste buildup seriously affecting raw material costs, but it was also posing an environmental hazard.

Danaher's priorities were two-fold. First, it wanted to upgrade the performance and reliability of its end-of-pipe waste treatment systems to ensure consistent compliance with environmental standards. Second, it wanted to reduce it's compliance costs.

After an evaluation of different nickel recovery systems was complete, Danaher chose Eco-Tec's Recoflo System. Besides savings in nickel, treatment chemicals, and sludge disposal, the Recoflo System could help them lower the nickel in their final effluent. This provided a greater safety margin between typical effluent concentration and allowable limits. Consequently, this system could save them money while at the same time allowing them to meet and exceed environmental regulations.

Intent on understanding all of its clients' needs and concerns, Eco-Tec worked with Danaher to complete a survey form designed to provide Eco-Tec with details about Danaher's operations. Based on that survey, Eco-Tec was able to select the most suitably sized unit, and advise Danaher engineers on installation of the Recoflo System.

With its patented ion exchange process, the Recoflo System offers optimum efficiency by recovering a sulfate/chloride balanced concentrate at a pH suitable for recycle, while rejecting brighteners, addition agents and sodium. In the first five months of operation, the System recovered 10,115 kg dry weight of nickel sulfate which exceeded original projections. From September, 1996 to April, 1999, Danaher has saved over $415,000 U.S. (Rs. 17,845,000) by

"I have roughly 30 years in the industry, and the way Eco-Tec questioned me about space, and covered all the details, was better than most of the vendors I have dealt with in that time....This recovery level exceeds the original projections by Eco-Tec and, of course, pleases Danaher management."

Samuel D. Craig
CEF Senior Process Engineer

recovering its nickel. Danaher estimates that it will eliminate approximately 29 tonnes of generated solid waste per year.

3. Recovery and purification of chromic acid

In decorative applications, chrome is what people see. In functional finishes, chrome is what does the work. In either case, a high quality finish is essential. While chrome plating solutions are not extremely sensitive, the accumulation of dissolved metals in the solution can lead to pitting and burning of the finish. Trivalent chrome can be oxidized back to the hexavalent form by reverse etching, but other metals such as iron and copper must be removed by dumping or some form of purification process.

In decorative lines, only about 5-10 % of the chromic acid purchased actually gets plated on the parts. The balance is lost to rinses and fume scrubbers. This represents a tremendous waste of material. In addition, chrome is one of the most highly regulated heavy metals. It's discharge to waterways is not permitted.

The costs associated with defects in surface coatings, material loss and environmental compliance compel platers to purify and recover chromic acid.

3.1 Effect of contaminants

Over time, baths become contaminated from the dissolution of a small amount of the metal piece being plated. These dissolved metal contaminants lower the throwing power of the bath and limit the current densities. The result is a slower plating bath that consumes more energy. Typical metallic contaminants include:

i) ***Trivalent chromium*** - Trivalent chromium formation is accelerated when plating with large cathode-to-anode ratios. It is also formed by the oxidation of oil, paint and grease. Trivalent chromium leads to 'treeing' effects in high current density areas. This can lead to chips during subsequent grinding or polishing steps. High levels of trivalent chromium also reduce solution conductivity (increasing voltage requirements) and cause dull deposits.

ii) ***Iron*** - iron accumulation in the plating bath can lead to the following:
- increased resistance to flow of current,
- decreased bright range,
- increased tendency to burn,
- rough and pitted deposits,
- reduced adhesion and brittleness of the chromium deposit (> 11 g/L).

iii) ***Other metals*** - performance can be hindered by the presence of other metals, namely:
- copper - more detrimental effect than iron,
- zinc - causes hazy deposits,
- aluminum, nickel and tin - individually not as detrimental as iron but, taken together, have an similar effect.

Short term solutions to counteract the effect of these metallic contaminants include:
- increasing the temperature of the bath solution
- increase the hexavalent chromium concentration,
- increase the solution agitation,
- bath dummying.

These are effective as short term measures, however, partial or complete disposal of the bath is often ultimately required. Figure 2 shows the negative effect that increasing iron levels can have on chrome plated parts.

3.2 Chrome purification alternatives

Over the past 15 years, purification of chromic acid plating solutions has predominantly been accomplished by either electrolytic or ion exchange methods. While porous pots have been used, most newer electrolytic methods use ion exchange membranes. Most ion exchange systems for chrome purification are based on the Recoflo ion exchange process.

The electrolytic approach offers the advantage of re-oxidizing trivalent chrome back to the useful hexavalent form. For most platers, however, trivalent chromium is easy to re-oxidize by dummying the bath. Problems associated with electrolytic systems include:

- Poor removal of other metallic contaminants. In fact, as other metals increase in concentration, the trivalent chrome re-oxidation efficiency is reduced,
- Membranes represent a large percentage of the overall system cost, so replacement costs are a considerable component of the overall operating costs,
- Electrolytic systems generate a waste - either spent catholyte solution or metallic oxide sludge, or both. Removing this material or solution can be a difficult and potentially hazardous procedure.

Electrolytic systems are best suited to applications where trivalent chrome is the predominant source of contamination, for example, chromic acid etching of plastic or plating inside tubes. Conversely, cation exchange systems appear better suited to larger operations, in particular those that have significant levels of metals besides trivalent chrome. Hard chrome plating, chromic acid anodizing, and closed-loop decorative plating are in this category. Table 3 summarizes the comparison of these two technologies.

3.3 The advanced ChromaPur System for chrome purification

A ChromaPur System uses the Recoflo equipment design principles to improve the performance of cation exchange resin. ChromaPur can remove up to 90% of the dissolved metals from concentrated chromic acid solutions. It incorporates a Recoflo cation exchange bed on a stainless steel frame, with an automated control and valving system.

ChromaPur can operate at two levels. When contaminant levels are high in the chromic acid (i.e., just after ChromaPur is installed), the loading cycle is shortened to provide a higher metals removal capacity. When the metals level has reach a low level in the plating solution, the loading cycle is lengthened to reduce regenerant chemical use.

The design of the regenerant system is a key feature of the ChromaPur System. Although, it would be more efficient to use hydrochloric acid for regeneration, chloride is a serious contaminant in chrome plating solutions that is difficult to remove. ChromaPur uses sulfuric acid to regenerate the resin. The acid is diluted automatically in the ChromaPur unit to the ideal level. The volume of regenerant pumped through the resin is precisely controlled to avoid wastage.

The ChromaPur is a reliable and economical method for chromic acid purification. Table 4 compares the costs of waste treatment and disposal to the ChromaPur.

ChromaPur Unit for continuous purification of hard chrome plating baths

3.4 Case Study - Boomsnub Corporation

Boomsnub Corporation, based in the United States, has been operating in the paper, printing and nuclear industries since the 1950's. Their business includes boomsnub manufacture (a hydraulic safety device for cranes), and job-shop, hard chrome plating.

During an expansion several years ago, Boomsnub was under a lot of scrutiny to comply with environmental regulations. As part of its solution, Boomsnub built a closed-loop system for its plating tanks to minimize hazardous emissions. The problem with the system, however, was that by reusing all the water, metallic contamination began to quickly accumulate. If not addressed, the contaminants would lead to quality problems.

> *"After comparing all the different alternatives, it became obvious to us that the Eco-Tec system was the only one that would help us accomplish what we wanted. Not only would it reduce our material and waste treatment costs, but it would also provide us with higher quality and fewer defects."*
>
> ***Traci Rohde***
> ***Certified Hazardous Materials Manager***

Boomsnub conducted a full scale comparison of all the different systems available - from porous pots, and membrane techniques, to dumping the baths, or simply letting the metal build-up. All of these different systems had drawbacks. Porous pots had high power costs, could not remove contaminants to low levels, took up valuable space in the plating bath, and required daily cleaning and maintenance. Electrolytic membrane units were unable to remove all metallic contaminants. In the end, the best choice was Eco-Tec's ChromaPur system. The ChromaPur system was able to remove all the contamination so the chromic acid could be reused. This eliminated waste treatment and haulage costs. Additionally, since the purified plating baths operate more efficiently, the electrical costs have been reduced.

3.5 Chrome rinse recovery

For decorative plating lines, a major issue is recovering chromic acid from the rinses. However, continuously recycling rinse-water to the plating bath will lead to a build-up of contaminants and the problems described above. Therefore, an effective recycling system will include both recovery and purification.

The most cost effective recycling scheme is to couple a ChromaPur system with an atmospheric evaporator. The ChromaPur system would be used for purifying the chromic acid. The atmospheric evaporator would be used for concentrating and allowing the return of the purified chromic acid.

Modifications of the above scheme are possible and have been used effectively to purify the bath, recover chromic acid and to recover rinse water for reuse.

4. Summary

Excellent opportunities are available to the platers to improve their operations. Recycling chromic acid and nickel salts are two excellent ways to reduce plating costs and environmental liabilities. With Recoflo Systems for nickel and chrome, recovered chemicals can be recycled with confidence that plating performance will not be negatively affected. In certain cases, improvements in plating performance are even possible.

Table 1: Comparison of nickel recovery processes

Feature	Recoflo System	Evaporator	Reverse osmosis	Electro-dialysis	Ion exchange	Electro-winning
Process						
-product concentr'n (g/L)	30-40	>40	10-20	10-20	10-15	n/a
-product pH ≈ 4.0	✓	✓	✓			n/a
-brightener rejection	✓			✓	✓	
-sodium rejection	✓				✓	✓
-removal to ppm level	✓	✓		✓	✓	
-insoluble anode	✓					
->99% recovery	✓			✓		
Economics						
-cost savings	3	1-2	2	2	1-2	1
-capital cost	2	1-3	2	2	2	2-3
-operator requirement	1	2	2	2	2	3
Track Record						
- in bright nickel recovery	✓	✓	✓	✓	✓	✓
- with OEM duplex nickel	✓					

Table 2: Typical economic benefits of the Recoflo System

Component	Waste disposal		Recoflo System	
Nickel salt (sulfate + chloride) Rs. 165/kg	20,000 kg	Rs. 3,300,000	200 kg	Rs. 33,000
32% Hydrochloric acid Rs. 4,000/tonne	-		2,000 kg	Rs. 8,000
93% Sulfuric acid @ Rs. 6,000/tonne	-		9,000 kg	Rs. 54,000
100% Caustic soda Rs. 25,000/tonne	6.3 tonne	Rs. 157,500	7.5 tonne	Rs. 187,500
10% sludge @ Rs. 500/tonne	75 tonne	Rs. 37,500	0.75 tonne	Rs. 375
Plant water @ Rs. 10.00/m^3	45,000 m^3	Rs. 450,000		
Deionized water @ Rs. 15.00/m^3	-		5,400 m^3	Rs. 81,000
Total cost	Rs. 3,945,000		Rs. 363,875	
Savings per year			Rs. 3,581,125	

Table 3: Comparison of chrome purification processes

Feature	Recoflo System	Electrolytic
Process		
- removes all metallic contaminants	✓	
- oxidizes Cr^{3+} to Cr^{6+}		✓
- fully automated	✓	
- easy to monitor	✓	
- compatible with fluoride-based catalyst baths	✓	
- compatible with high-efficiency etch-free chemistry	✓	
Economics (1-low, 2-moderate, 3-high)		
- capital cost	1	1-3
- operating costs	1	1
- replacement parts / servicing cost	1	3
Track record		
- widely used in decorative and functional applications	✓	

Table 4: Economic comparison of chrome bath treatment alternatives.

Item	Recoflo System	On-site treatment	Off-site disposal
Bath Replacement	-	Rs. 150,500	Rs. 150,500
Chemicals	Rs. 23,177	Rs. 74,605	-
Solids Disposal	Rs. 5,977	Rs. 57,663	-
Liquid Disposal	-	-	Rs. 344,000
Total Costs	Rs. 29,154	Rs. 282,768	Rs. 494,500

Basis: 3,785 liter bath volume; 240 g/L chrome; 15 g/L metals.

Figure 1: S.T.E.P. test results when recycling nickel salts recovered by a Recoflo System.

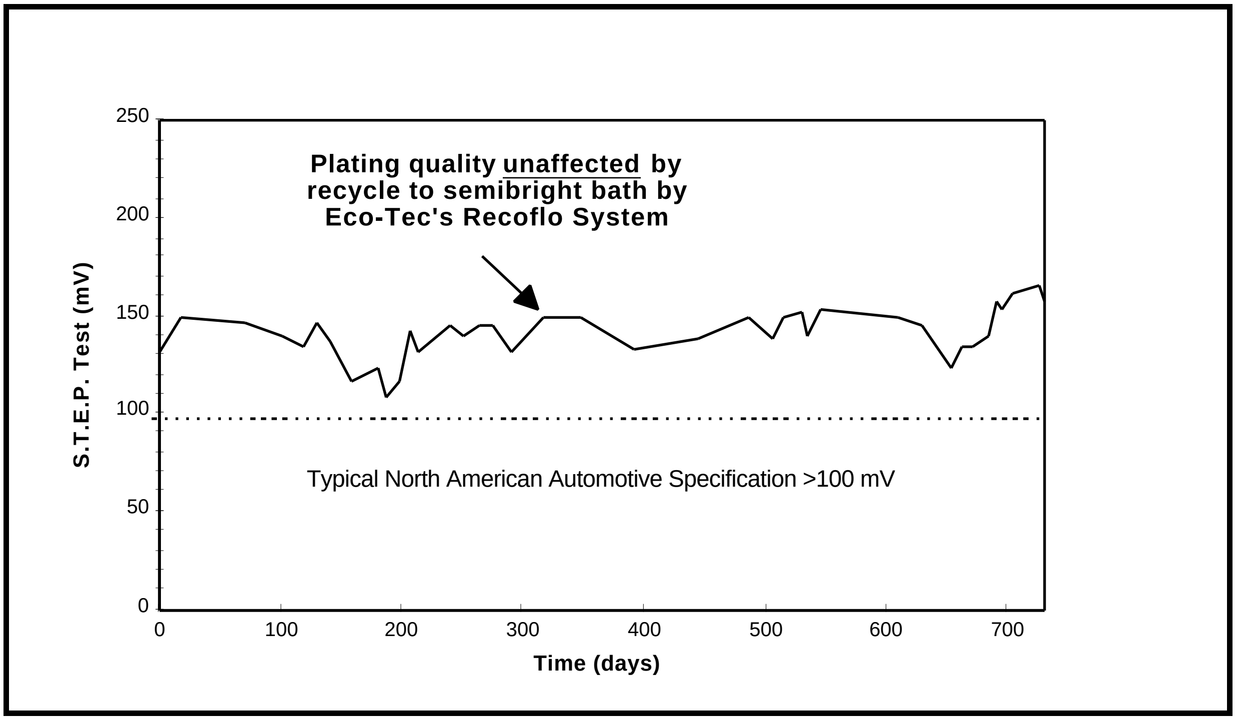

Figure 2: Effect of iron level on chrome plating defects